

Heterogeneous Reaction of
 $\text{ClONO}_2 (\text{g}) + \text{NaCl} (\text{s}) \rightarrow \text{Cl}_2 (\text{g}) + \text{NaNO}_3 (\text{s})$

Raimo S. Timonen*, Liang T. Chu**, Ming-Taun Leu***, and Leon F. Keyser
Earth and Space Sciences Division, Jet Propulsion Laboratory, California
Institute of Technology, Pasadena, California 91109

Abstract

The heterogeneous reaction of $\text{ClONO}_2 + \text{NaCl} \rightarrow \text{Cl}_2 + \text{NaNO}_3$ (1) was investigated over a temperature range of 220 - 300 K in a flow-tube reactor interfaced with a differentially pumped quadrupole mass spectrometer. Partial pressures of ClONO_2 in the range 10^{-8} - 10^{-5} Torr were used. Granule sizes and surface roughness of the NaCl substrates were determined by using a scanning electron microscope; and in separate experiments, surface areas of the substrates were measured by using BET analysis of gas-adsorption isotherms. For dry NaCl substrates both the decay rates of ClONO_2 and the growth rates of Cl_2 were used to obtain reaction probabilities, $\gamma_1 = (4.6 \pm 3.0) \times 10^{-3}$ at 298 K and $(6.7 \pm 3.2) \times 10^{-3}$ at 225 K, after considering the internal surface area. The error bars represent one standard deviation. The Cl_2 yield based on the ClONO_2 reacted was measured to be 1.0 ± 0.2 . In order to mimic the conditions encountered in the lower stratosphere, the effect of water vapor pressures between 5×10^{-5} and 3×10^{-4} Torr on reaction (1) was also studied. With added H_2O , reaction probabilities, $\gamma_1 = (4.1 \pm 2.1) \times 10^{-3}$ at 298 K and $(4.7 \pm 2.9) \times 10^{-3}$ at 225 K, were obtained. A trace of HOCl , the reaction product from the $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$ reaction, was observed in

addition to the C12 product from reaction 1. The implications of this result for the enhancement of hydrogen chloride in the stratosphere after the El Chichon volcanic eruption and for the marine troposphere are discussed.

*Current address: Department of Physical Chemistry, University of Helsinki, SF-00170, Helsinki, Finland.

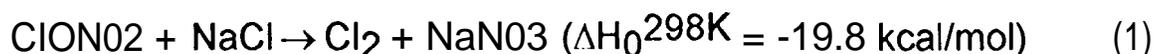
**Current Address: Department of Environmental Health and Toxicology, Wadsworth Center for Laboratory Research, State University of New York, P. O. Box 509, Albany, New York 12201.

***To whom correspondence should be addressed.

(naclrev.doc:1-1 1-94)

1. Introduction

The heterogeneous reaction of gaseous chlorine nitrate and solid sodium chloride



is of potential importance in atmospheric chemistry. NaCl particles about 2 micrometers in size were collected by a crystal-balanced cascade impactor from the El Chichon eruption cloud in the lower stratosphere during April and May 1982 [1]. Simultaneous infrared spectral measurements of the hydrogen chloride column density in the volcanic cloud [2] showed enhancements by as much as 40 percent over background. Direct injection of HCl into the stratosphere failed to produce an overall HCl increase three months after the volcanic eruption because the chemistry was perturbed in a single pulse and the large gradient in HCl was quickly smoothed out by diffusion [3,4]. Furthermore, it has been suggested that HCl should be washed out rapidly in the troposphere [5]. Several heterogeneous reactions, including reaction (1), have been suggested to explain this important observation [4]. It is well known that an enhancement of the chlorine budget, for example, the emission of anthropogenic chlorofluoromethanes, can influence the catalytic destruction of ozone in the stratosphere.

Heterogeneous reactions on the surfaces of sea-salt aerosol, for example reaction (1), have also been suggested as a potential source of atomic chlorine in the marine boundary layer [6-9]. Sea-salt aerosol is generated by breaking waves on the ocean's surface. Oxidation by active chlorine may represent a significant sink for alkanes and dimethylsulfide

(DMS). In addition, a chain reaction involving ClO_x and HO_x radicals could provide either a source or a sink for ozone, depending on NO_x levels.

There is one previous mechanistic study of reaction (1). Finlayson-Pitts et al. [7] employed both mass spectrometry and ultraviolet spectrometry. Partial pressures of ClONO_2 about $(1.2 - 3.7) \times 10^{-2}$ were allowed to react with the NaCl particles which were packed in a cylindrical cell at room temperature. The partial pressures used are several orders of magnitude greater than those in the atmosphere. The residence time of the ClONO_2 in the cell was approximately 5-10 s; this is significantly longer than the time scale used in the present flow-tube experiments. The Cl_2 yield was estimated to be 40 %. No other reaction products were detected. Neither the reaction probability nor the effects of temperature and water vapor on reaction (1) were reported.

In this article we report the first measurement of the reaction probability, γ_1 , for reaction (1) using partial pressures of ClONO_2 (10^{-8} - 10^{-5} Torr) similar to those in the stratosphere. First, we will describe the experimental procedures used. Next we will summarize and discuss the results of NaCl deactivation and reaction probability measurements. Finally, we will discuss briefly the possible application of this work to understanding the HCl enhancement in the stratosphere after the El Chichon eruption.

II. Experimental Section

The reaction probability measurement was performed in a flow-tube reactor coupled to a differentially pumped quadrupole mass spectrometer.

The details of the apparatus have been discussed in our previous publications [1 O-14] and we will only briefly describe it in this article.

Flow Reactor. The flow reactor was made of borosilicate glass, and its dimensions are 20.0 cm in length and approximately 2.2 cm inside diameter (see Figure 1). The bottom of the reactor was flattened in order to hold the NaCl substrates in place. The reactant, for example ClONO₂, was admitted into the reactor through five fixed inlets; they are separated by 2.5 cm. The temperature of the reactor was controlled by a refrigerated bath and measured by a thermocouple attached to the middle section. The pressure inside the reactor was monitored by a high-precision capacitance manometer (MKS Instruments, Model 390HS, 10 Torr full scale) which was located about 4 cm from the reactor at the downstream end. The measured pressure was corrected (<8%) for the viscous pressure drop between the measurement point and the midpoint of the reactor. A total pressure of 0.30 Torr was used in the flow reactor.

ClONO₂ Synthesis and Calibration. ClONO₂ was synthesized by mixing a small amount of Cl₂O with N₂O₅ at 195 K; the mixture was allowed to warm to 248 K in order to increase the ClONO₂ yield. This procedure was repeated several times. The ClONO₂ thus prepared was further purified by vacuum distillation at 195 K and 178 K. The Cl₂ impurity was found to be small (<1%); thus, it is not likely to interfere our reaction probability measurements (see next section). Vapor pressures of ClONO₂ in the reservoir were measured by a high precision pressure meter (MKS Instruments, Model 390HS, 1 Torr full scale). During the experiment, helium was bubbled through the ClONO₂ reservoir which was maintained at 155 K or higher, depending on the ClONO₂ concentrations required in the experiment. The low temperature bath was prepared by mixing liquid

nitrogen with either methanol or ethanol. The helium gas saturated with ClONO₂ was admitted to the flow reactor.

Preparation of the NaCl Substrates. NaCl crystals (>99.8% purity, analytical reagent) were supplied by either Baker or Mallinckrodt. The impurity levels of bromine or iodine compounds, which may react with ClONO₂, were stated to be less than 0.005% and 0.001 %, respectively. The size and shape of these crystals were examined by using a scanning electron microscope and electron micrographs of one sample used in these experiments are shown in Figure 2. The typical shape of the NaCl particles is cubic and the average size is about 0.48 μm. The BET specific surface area of these samples was found to be about 100 cm²/g. The specific surface area, S_g, was also calculated from the average crystal size by using eq 2 [15]

$$S_g = 6/\rho_t d \quad (2)$$

where ρ_t is the true density of NaCl (2.165 g/cm³) [16] and d is the particle size. Using d = 0.48 μm obtained from the SEM experiments, we obtain a surface area of 58 cm²/g from eq 2. The difference between this result and BET area is most likely due to the surface roughness which can be seen in Figure 2b. Another possibility is that there may be some internal cracks or pores within the crystals.

In some experiments the NaCl granules were ground in a procelain mortar and sieved by using mesh sizes 85 and 140. These samples were also examined by a scanning electron microscope (Figure 3). The average size is about 4 μm. The BET specific surface area was measured to be 7340 cm²/g. This result is in good agreement with the value of 6930 cm²/g

calculated from eq 2 and suggests that there are no internal pores nor significant roughness associated with the ground samples.

The NaCl substrates were prepared by using several methods in order to simulate the aerosol conditions encountered in the stratosphere after a volcanic eruption. In one set of the experiments the granules were baked at temperatures up to 473 K in the flow reactor overnight; the H₂O vapor pressure over these substrates was measured to be less than 2×10^{-5} Torr by using a mass spectrometer. In another set of the experiments, the granules were held in flow reactor and a stream of H₂O vapor was passed over the NaCl granules; the H₂O vapor pressure was kept in the range, $2 \times 10^{-5} - 3 \times 10^{-4}$ Torr. The thickness of the NaCl substrates inside the reactor was varied from 1.0 mm to 5.0 mm.

Procedures for the NaCl Surface Deactivation Measurements.

The reaction between ClONO₂ and NaCl forms C12 and NaNO₃. Cl₂ does not adsorb on the surface of NaCl; it desorbs into the helium carrier. However, the product NaNO₃ remains on the surface of NaCl and can block the reaction with ClONO₂. To determine the deactivation of the NaCl surface, both the loss of ClONO₂ and the yield of Cl₂ were measured over a period of several hours at 298 K and 225K. The results will be given in the next section.

Procedures for Reaction Probability Measurements. The reaction probability for (1) was determined as follows. The loss rate of ClONO₂ at m/e = 46 and the growth rate of C12 at m/e = 70 were measured as a function of inlet position, z. The reaction time was calculated by using $t = z/v$ where v is the average flow velocity. In each experiment we calculated the cross sectional area of the reactor and then the flow velocity. The first-order rate constant, k_s, was calculated from the slope of a linear least-

squares fit to the experimental data. The axial gas-phase diffusion correction for k_s was made by using the following equation [17,18]

$$k_g = k_s (1 + k_s D/v^2) \quad (3)$$

The diffusion coefficient of ClONO_2 in helium was estimated to be $pD = 354 \text{ Torr cm}^2\text{s}^{-1}$ at 298 K [19]. A temperature coefficient of $T^{1.75}$ for the diffusion coefficient was also assumed. The corrected rate is designated as k_g .

For the radial gas-phase diffusion, it is more difficult to estimate the correction to k_s because the reactor is no longer a fully symmetric cylindrical tube. If we use the full reactor radius of 1.1 cm in the calculation, the correction is relatively small, about 5-10 %. Since this correction is not precise, we neglected it in the data analysis.

Based on the geometric area, S , of the NaCl substrate and the volume, V , of the reactor, the reaction probability, γ_g , was then calculated by using the following equation [18]

$$\gamma_g = 4k_g V / \bar{v} S \quad (4)$$

where \bar{v} is the average molecular velocity for ClONO_2 . Note that this equation is valid for $\gamma_g < 0.1$ only, which holds for the present experiments.

In order to take the internal surface area into account, we used an analysis recently developed for heterogeneous reactions on ice surfaces [20,21]. We model the NaCl substrate as hexagonal close-packed (HCP) spherical granules stacked in layers. For this model, the following equation holds

$$\gamma_t = \gamma_g \pi^{-1} 3^{1/2} \{1 + \eta [2(N_L - 1) + (3/2) 1/2]\}^{-1} \quad (5)$$

where γ_t is the true reaction probability for reaction (1) and N_L is the number of granule layers or the ratio of the thickness of the NaCl substrates to the average granule size. In eq 5, η is the effectiveness factor, which is the fraction of the NaCl surface that participates in the reaction. This factor is determined by the relative rates of pore diffusion to surface reaction and is given by

$$\eta = \phi^{-1} \tanh \phi \quad (6)$$

$$\phi = (h/d) [3\rho_b/2(\rho_t - \rho_b)] (3\tau\gamma_t) \quad (7)$$

where h is the substrate thickness, d is the average size of granules, ρ_b is the bulk density, ρ_t is the true density and τ is a tortuosity factor. Typically, this factor is about 2 to 4 [22]. In our data analysis, we used a value of 2. This type of calculation has been used and discussed in previous publications [14,21].

III. Results and Discussion.

NaCl Surface Deactivation Measurements.

Typical NaCl surface deactivation data at 298 K are shown in Figure 4. The amount of ClONO₂ removed was obtained by integrating the calibrated ClONO₂ signal intensities over time. In this experiment the mass of NaCl is 15 g and the specific surface area is approximately 100 cm²/g (see Figure

2). Thus, the total surface area is about $1.5 \times 10^3 \text{ cm}^2$. The amount of ClONO_2 reacted is calculated to be about 1×10^{16} molecules/ cm^2 over a period of 6 hours without any sign of saturation. Another measurement was carried out using the ground NaCl substrate. (see Figure 3) The specific surface area of this sample is $7340 \text{ cm}^2/\text{g}$. The amount of ClONO_2 reacted is greater than 5×10^{15} molecules/ cm^2 . The average value of these two measurements is $> 7.5 \times 10^{15}$ molecules/ cm^2 .

Surface deactivation data taken at 225 K are shown in Figure 5. The mass of the NaCl substrate used is 6 g and the the specific surface area is $100 \text{ cm}^2/\text{g}$ (see Figure 2) The data show that at this temperature fully saturation is reached. We obtain a value of 5.7×10^{14} molecules/ cm^2 for the amount of ClONO_2 reacted. Another measurement was performed using the ground NaCl substrate with the specific surface area of $7340 \text{ cm}^2/\text{g}$ (see Figure 3). The result is 2.7×10^{14} molecules/ cm^2 of ClONO_2 reacted, The average value of these two measurements is 4.2×10^{14} molecules/ cm^2 , which is at least a factor of 18 smaller than that at 298 K.

It should be noted that the above measurements were performed using ClONO_2 pressures as high as 2×10^{-5} Torr. Experiments were also run at pressures less than 1×10^{-6} Torr, which are typical of the ClONO_2 pressures used to measure the reaction probability. (see the next section) At these lower pressures, the NaCl substrates are never completely deactivated after a few hours of contact with ClONO_2 and the amount of uptake (or surface deactivation) could not be accurately obtained.

The uptake of ClONO_2 on the surface of NaCl granules has been measured to be $> 7.5 \times 10^{15}$ molecules/ cm^2 at 298 K and 4.2×10^{14} molecules/ cm^2 at 225 K, respectively. The uptake is at least a factor of 18 lower at the lower temperature. Reaction (1) forms product NaNO_3 on the

surface of NaCl granules. If we assume that the cross-sectional area for each NaNO₃ molecule is 40×10^{-16} cm² [23], the data at 225 K suggest that the NaCl surface is covered by approximately a monolayer of NaNO₃. However, the data at 298 K suggest a coverage more than 18 layers of NaNO₃ molecules which we believe is unlikely. Alternatively, solid-phase diffusion of Na⁺ and NO₃⁻ ions in NaCl may play a role in the surface deactivation experiments because the diffusion of ionic species may be faster than the neutral species. [24,25] Furthermore, the diffusion coefficient is strongly temperature dependent; this may explain the effect of temperature on the surface deactivation. If we assume that the diffusion coefficient is 10^{-20} cm²/s, a typical value for solid state diffusion, and the contact time is 104 s, the penetration length could be estimated to be $\approx (4Dt)^{1/2} = 2 \times 10^{-8}$ cm. The penetration length is almost equal to the molecular diameter. However, these suggestions are considered as rather speculative and should be investigated in future experiments.

Based on calibrated mass spectrometer sensitivities, the amount of Cl₂ formed agrees well with the amount of ClONO₂ lost. In experiments using dry NaCl granules, no other products were detected mass spectrometrically. The measured stoichiometric ratio for reaction (1) is 1.0 ± 0.2 over the temperature range 225-298 K. The error represents the accuracy of calibration. However, when water vapor was present in the reactor, we detected the formation of HOCl in addition to Cl₂.

In recent experiments, Finlayson-Pitts et al. [7] reported that the Cl₂ yield for reaction (1) based on ClONO₂ reacted is 0.40; this is significantly smaller than the present result of 1.0 ± 0.2 . The discrepancy is probably due to the calibration procedures used for reactant (ClONO₂) and product

(Cl₂). They used an ultraviolet absorption technique while we employed mass spectrometric detection.

Reaction Probability Measurements.

For an irreversible pseudo-first-order reaction under plug-flow conditions, the following equation holds for the decay of ClONO₂

$$\ln [S(z)] = -k_S(z/v) + \ln [S(0)] \quad (8)$$

where $S(z)$ is the ClONO₂ signal when the inlet position is at z and $S(0)$ is the signal when the NaCl is bypassed (zero reaction). The corresponding equation for the growth of the Cl₂ signal, assuming rapid resorption from the surface, is given by

$$\ln [S(\infty) - S(z)] = \ln [S(\infty)] - k_S(z/v) \quad (9)$$

where $S(\infty)$ is the Cl₂ signal when the reaction has reached completion. The left-hand sides of eqs (8) and (9) are plotted vs the reaction time, z/v , for the reactant decay and the product growth, respectively. Observed reaction rate constants, k_S , are determined from linear-least-squares fits to these data.

The reaction probability for reaction (1) was measured by observing the decay of ClONO₂, monitored at $m/e = 46$ as a function of inlet position. In a separate run using the same NaCl substrate immediately after the ClONO₂ decay measurement, the formation of Cl₂ at $m/e = 70$ was also monitored as a function of the inlet position. A typical set of data is shown in Figure 6. The initial ClONO₂ concentration used in this experiment is $5.9 \times$

10⁻⁷ Torr. The mass of NaCl was 15 g and the temperature of the flow reactor was 296 K. Both the decay of ClONO₂ and the growth of Cl₂ were observed.

The experimental conditions used in the determination of the reaction probability are summarized in Table 1. The measured reaction probabilities have been corrected for external gas-phase diffusion and internal surface areas as discussed in the previous section. The results are summarized in Table 2. We obtain average values of $\gamma_t = (4.63 \pm 3.05) \times 10^{-3}$ at 298 K and $(6.73 \pm 3.17) \times 10^{-3}$ at 225 K for the dry samples of NaCl. These results are obtained by using only the first set of reaction probability measurements in a given run. The first measurements are considered more reliable because the contact time is still relatively short and the surface deactivation is not serious. The uncertainties represent one standard deviation. The results indicate a small temperature dependence between 225-298 K.

Some experiments were performed in the presence of H₂O vapor pressures about 5.7×10^{-5} - 3.0×10^{-4} Torr. We obtained similar results as shown in Figure 6 except a small signal of HOCl being formed in addition to the much larger Cl₂ signals. Both the experimental conditions and the reaction probabilities measured are summarized in Tables 1 and 2. The results are $\gamma_t = (4.07 \pm 2.10) \times 10^{-3}$ at 298 K and $(4.72 \pm 2.87) \times 10^{-3}$ at 225 K. The uncertainties represent one standard deviation. The result obtained from ClONO₂ decay at 225 K is considered to be unreliable because of interference at $m/e = 46$ from HN₃ product. The ClONO₂ + H₂O → HOCl + HN₃ reaction is faster at 225 K than that at 298 K because of the adsorption of H₂O molecules on the NaCl surfaces. Therefore, for the experiments using the unbaked sample with water vapor at 225 K this result is not considered in the determination of γ_t .

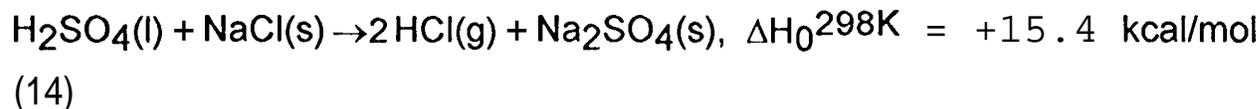
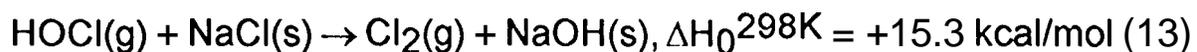
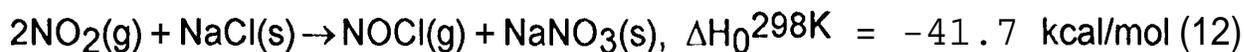
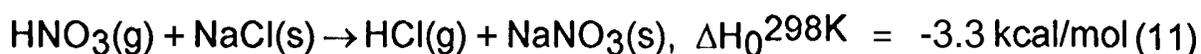
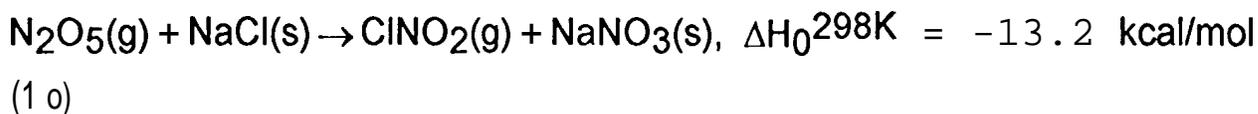
In one experiment a large amount of water vapor about 3×10^{-3} Torr was used. (see Table 1) The yield of Cl_2 is much smaller than the yield of HOCl . This result is not considered in the determination of γ_t for reaction (1). In other experiments the same procedure was also repeated in the absence of NaCl substrates at both 298 K and 225 K. The first-order rate constant for the ClONO_2 decay is much smaller than that reported in Table 1. The observation is probably due to the reaction of ClONO_2 with a trace of water molecules adsorbed on the wall of the flow reactor. Nevertheless, a trace of HOCl signal was observed in these experiments. No correction is required for this background wall loss.

This is the first determination of the reaction probability for reaction (1). The average value of γ_t is $(4.6 \pm 3.0) \times 10^{-3}$ at 298 K and $(6.7 \pm 3.2) \times 10^{-3}$ at 225 K for dry NaCl substrates. This suggests that the temperature dependence is slightly negative. In the presence of water vapor pressures between 5.7×10^{-5} and 3.0×10^{-4} Torr we obtain a value of $\gamma_t = (4.1 \pm 2.1) \times 10^{-3}$ at 298 K and $(4.7 \pm 2.9) \times 10^{-3}$ at 225 K. These values are slightly less than those obtained with dry NaCl substrates. In addition, the Cl_2 yield based on ClONO_2 reacted is about unity. The γ value for the analogous reaction of $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$ on ice surfaces or nitric acid trihydrate surfaces at 190-220 K is about 0.1 as recently determined in this laboratory [10,14] and elsewhere [26,27]. This large difference in reactivity (\sim a factor of 20) maybe due to the temperatures of flow-tube reactors used in these studies or details in the surface morphology of the solid substrates.

Implications for the lower stratosphere and marine troposphere.

As discussed in the Introduction Section, in addition to reaction (1), several heterogeneous reactions have been proposed between solid NaCl

and a gaseous species to form active chlorine potentially important in atmospheric effects after El Chichon eruption. These reactions are given as follows:

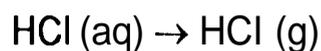
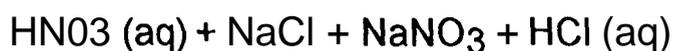
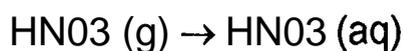
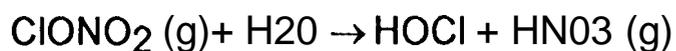


The enthalpy of reaction (14) is calculated for an acidic solution of 75 wt% H₂SO₄, a typical composition in the lower stratosphere, using literature values [16]. For more concentrated sulfuric acid (greater than 75 wt%), the enthalpy may be negative and reaction (14) may proceed rapidly. Recent experiments suggested that γ for reaction (10) is $> 0,005$ and that γ for reaction (12) is less than 10^{-8} at 298 K. In unpublished work [28] we obtain a value of $\gamma > 0.002$ at 220 K for reaction (11). Since both reactions (13) and (14) are endothermic by about 15 kcal/mol, we assume the reaction probabilities are negligible. Moreover, the measured reaction probability [29] for reaction (12) is too slow to be of importance. For reaction (1) we

adopt a value of 0.005 based on the experimental data discussed in the previous section.

Heterogeneous reaction rates for reactions (1), (10) and (11) can be calculated by using the following equation $v = 1/4\gamma\bar{v}AN$ where \bar{v} is the mean molecular velocity, A is the mean surface area for each NaCl particle, and N is the number density of NaCl particles (26 particles per cm³ at 28 km) [4]. We obtain rates for reactions (1), (10) and (11): $> 5.7 \times 10^{-5} \text{ s}^{-1}$, $> 5.4 \times 10^{-5} \text{ s}^{-1}$ and $> 1.4 \times 10^{-5} \text{ s}^{-1}$, respectively. These rates are comparable to those for gas-phase homogeneous reactions or photolytic reactions as discussed by Michelangelo et al.[4] Thus, these reactions can provide a permanent sink for NO_x and also can produce Cl_x, forming HCl through photochemical reactions. These simple calculations assume that these reactions take place without NaCl surface deactivation, which was observed in the laboratory experiments, particularly at lower temperatures near 220 K. Therefore, accurate assessment of atmospheric importance needs to consider the effect of surface deactivation of the NaCl particles in the volcanic clouds. A detailed numerical study will be needed to address this issue.

In the marine troposphere, sea-salt aerosol is generated by breaking waves on the ocean's surface and is most likely comprised of liquid droplets. The relative humidity is expected to be high as compared with the ambient conditions in the lower stratosphere. Thus, our present results using dry NaCl particles or the salt particles in the presence of water vapor pressures about 10⁻⁵ - 10⁻³ Torr cannot be directly applicable to the marine troposphere. However, the evidence presented in the previous section suggests that under relatively high-humidity conditions the reaction sequence for reaction (1) may proceed as follows:



As noted by Keene et al. [8] this reaction scheme is probably of minor importance in the observation of HCl formation and the Cl⁻ deficits in sea-salt aerosols. Photochemistry in the marine boundary layer is very complex and several other mechanisms presented in the literature [8] are needed for a complete understanding. A detailed discussion is beyond the scope of this paper,

Acknowledgement. The research described in this article was performed at the Jet Propulsion Laboratory, California Institute of Technology under a contract with the National Aeronautics and Space Administration. R.S.T. gratefully acknowledges the financial support from Imatran Voima Foundation, and also from Maj and Tor Nessling Foundation. We are grateful to Prof. Yuk L. Yung for useful discussions.

References and Notes

1. Woods, D. C.; Chuan, R. L.; Rose, W. 1. *Science*, 1985, 230, 170.
2. Mankin, W. G.; Coffey, M. T. *Science*, 1984, 226, 170.
3. Michelangelo, D. V.; Allen, M.; Yung, Y. L. *J. Geophys. Res.* **1989**, 94, 18429.
4. Michelangelo, D. V.; Allen, M.; Yung, Y. L. *Geophys. Res. Lett.* **1991**, **18**, 673.
5. **Pinto, J. P.**; Turco, R. P.; Toon, O. B. *J. Geophys. Res.* 1989, 94, 11165.
6. Finlayson-Pitts, B. J. *Nature* **1983**, **306**, 676.
7. **Finlayson-Pitts, B. J.**; Ezell, M. J.; Pitts, J. N., Jr. *Nature* 1989, 337, 241.
8. Keene, W. C.; Pszenny, A. A. P.; Jacob, D. J.; Duce, R. A.; Galloway, J. N.; Schultz-Tokos, J. J.; Sievering, H.; Boatman, J. F.; *Global Biogeochem. Cycles*, **1990**, 4,407.
9. Pszenny, A. A. P.; Keene, W. C.; Jacob, D. J.; Fan, S.; Maben, J. R.; Zetwo, M. P.; Springer-Young, M.; Galloway, J. N. *Geophys. Res. Lett.* **1993**, **20**,699.
10. **Leu, M.-T.** *Geophys. Res. Lett.* **1988**,**15**, 17.
11. Leu, M.-T.; Moore, S. B.; Keyser, L. F. *J. Phys. Chem.* **1991**, **95**, 7763.
12. **Leu, M.-T.**; Blamont, J. E.; Anbar, A. D.; Keyser, L. F.; Sander, S. P. *J. Geophys. Res.* 1992, 97,2621.
13. Chu, L. T.; Leu, M.-T.; Keyser, L. F. *J. Phys. Chem.* 1993, 97, 7779.
14. Chu, L. T.; Leu, M.-T.; Keyser, L. F. *J. Phys. Chem.* 1993, 97, 12798.
15. Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, Academy Press, New York (1982).

16. Weast, R. C. *Handbook of Chemistry and Physics*, CRC Press, 65th Edition (1984).
17. Walker, R. E. *Phys. Fluids*, 1961, 4, 1211,
18. Kaufman, F. *Prog. Read. Kinet.* 1961, 1, 1.
19. Marrero, T. R.; Mason, E. A. *J. Phys. Chem. Ref. Data*, 1972, 1, 3.
20. Keyser, L. F.; Moore, S. B.; Leu, M.-T. *J. Phys. Chem.* **1991**, 95, 5496.
21. Keyser, L. F.; Leu, M.-T.; Moore, S. B. *J. Phys. Chem.* 1993, 97, 2800.
22. Satterfield, C. N. *Heterogeneous Catalysis in Industrial Practice*, Second Edition, McGraw-Hill, Inc. (1991).
23. McClellan, A. L.; Harnsberger, H. F. *J. Colloid Interface Sci.* **1967**, 23, 577.
24. Barrer, R. M. *Diffusion in and Through Solids*, Cambridge University Press (1951).
25. Hannay, N. B. *Solid State Chemistry*, Prentice-Hall, Englewood, New Jersey (1967).
26. Abbatt, J. P. D.; Molina, M. J. *J. Phys. Chem.* **1992**, 96, 7674.
27. Hanson, D. R.; Ravishankara, A. R. *J. Geophys. Res.* **1991**, 96, 5081.
28. Timonen, R.; Leu, M.-T., unpublished data, 1993.
29. Livingston, F. E.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **1991**, 78, 17.

Figure Captions

Figure 1. Schematic diagram of the experimental apparatus. Inlets 1-6 are for the injection of ClONO_2 .

Figure 2. Scanning electron micrographs of NaCl granules. (a) a magnification factor of 20. (b) a magnification factor of 1000. The specific surface area has been measured to be about $100 \text{ cm}^2/\text{g}$. The average granule size is 0.48 mm in diameter. See text for details.

Figure 3. Scanning electron micrographs of ground NaCl granules. (a) a magnification factor of 20. (b) a magnification factor of 1000. The specific surface area has been measured to be about $7340 \text{ cm}^2/\text{g}$. The average granule size is $4 \mu\text{m}$. See text for details.

Figure 4. Surface deactivation measurement on a NaCl substrate at 296 K. The experimental conditions are: $[\text{ClONO}_2] = 2.65 \times 10^{-5} \text{ Torr}$, total pressure = 0.302 Torr, weight of NaCl = 15 g, and the specific surface area is $100 \text{ cm}^2/\text{g}$. ○, NaCl bypassed; ●, NaCl in contact with ClONO_2 ; (a), the loss of ClONO_2 ; (b) the formation of Cl_2 .

Figure 5. Surface deactivation measurement on a NaCl substrate at 225 K. The experimental conditions are: $[\text{ClONO}_2] = 1.8 \times 10^{-5} \text{ Torr}$, total pressure = 0.283 Torr, weight of NaCl = 6 g, and the specific surface area = $100 \text{ cm}^2/\text{g}$. ○, NaCl bypassed; ●, NaCl in contact with ClONO_2 ; (a), the loss of ClONO_2 ; (b) the formation of Cl_2 .

Figure 6. Reaction probability measurement for reaction (1). The experimental conditions are: $[\text{ClONO}_2] = 5.9 \times 10^{-7}$ Torr, $P = 0.283$ Torr, $[\text{H}_2\text{O}] = 5.7 \times 10^{-5}$ Torr, weight of NaCl = 15 g, and $T = 296$ K. Closed circles are for the decay of ClONO_2 . Open circles are for the growth of Cl_2 .

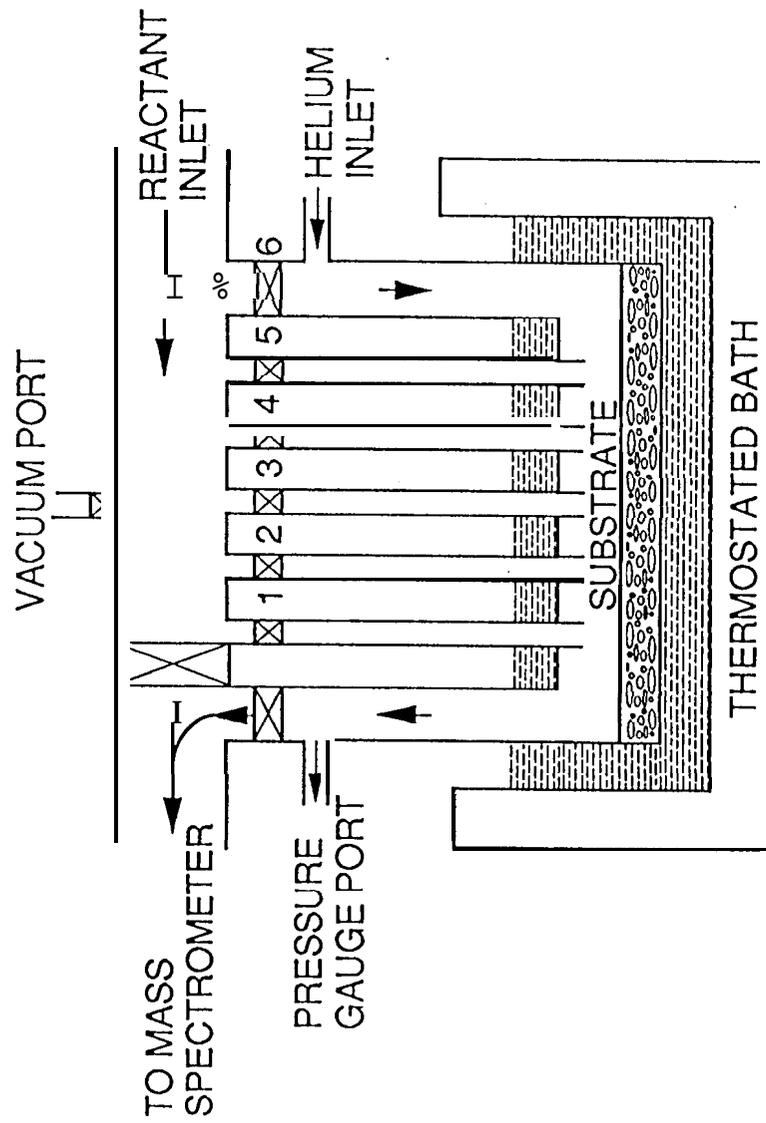
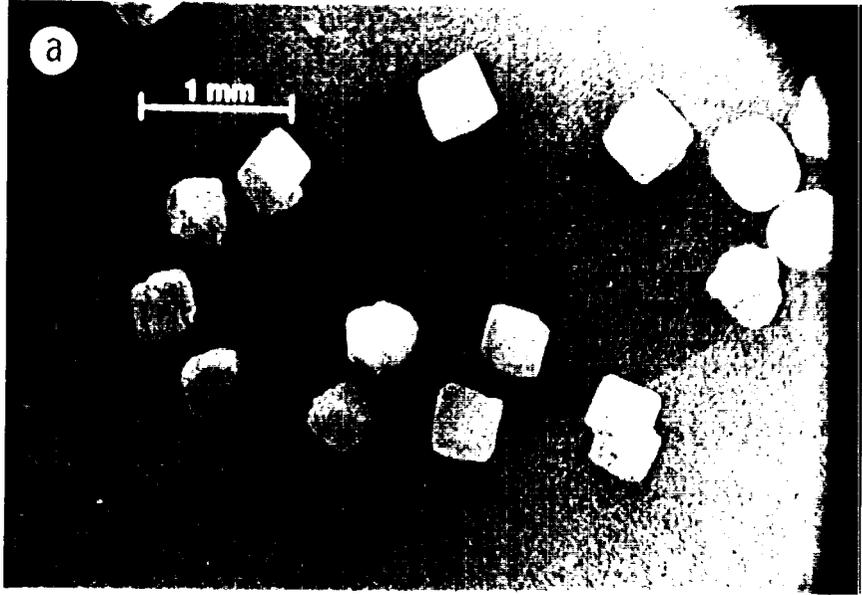
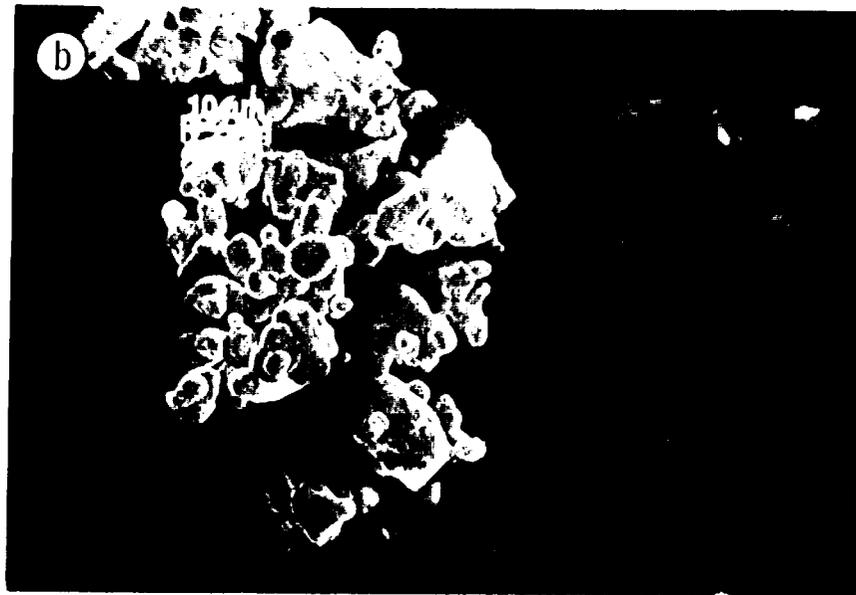
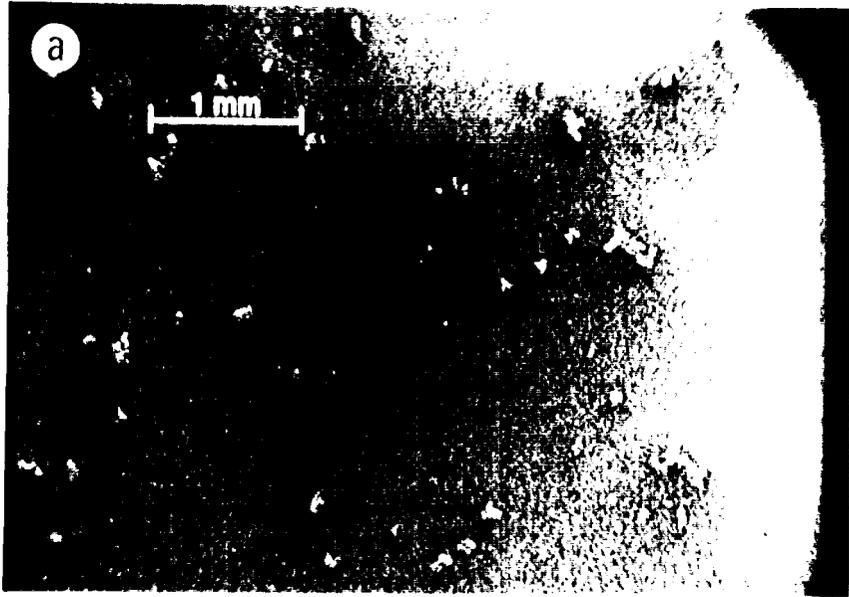


Fig. 1





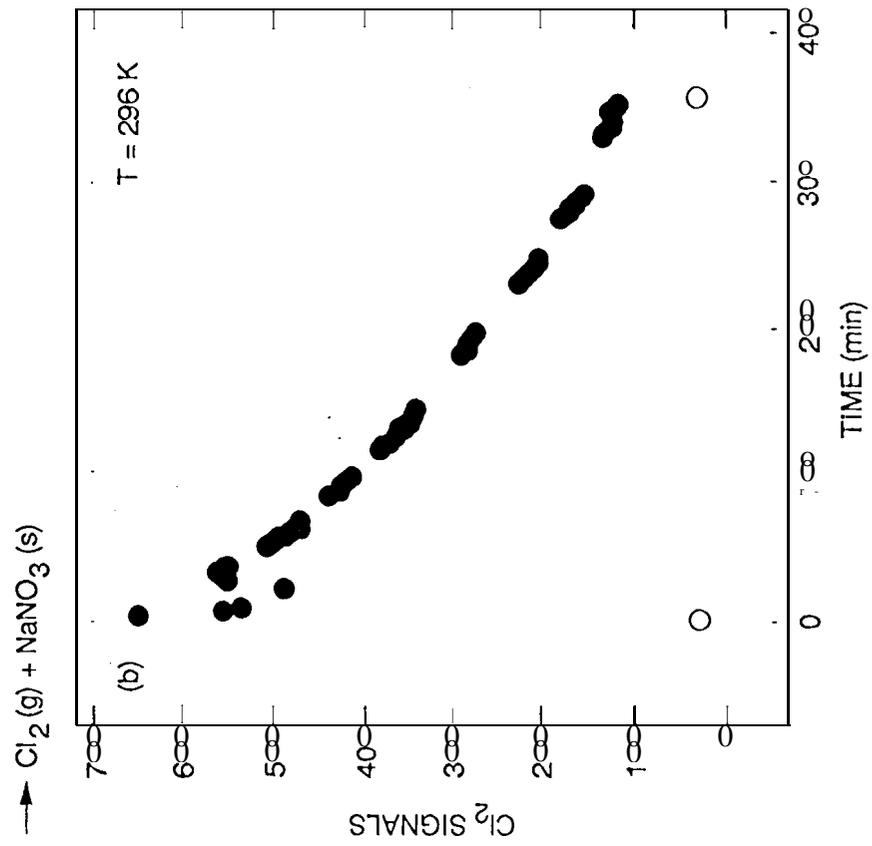
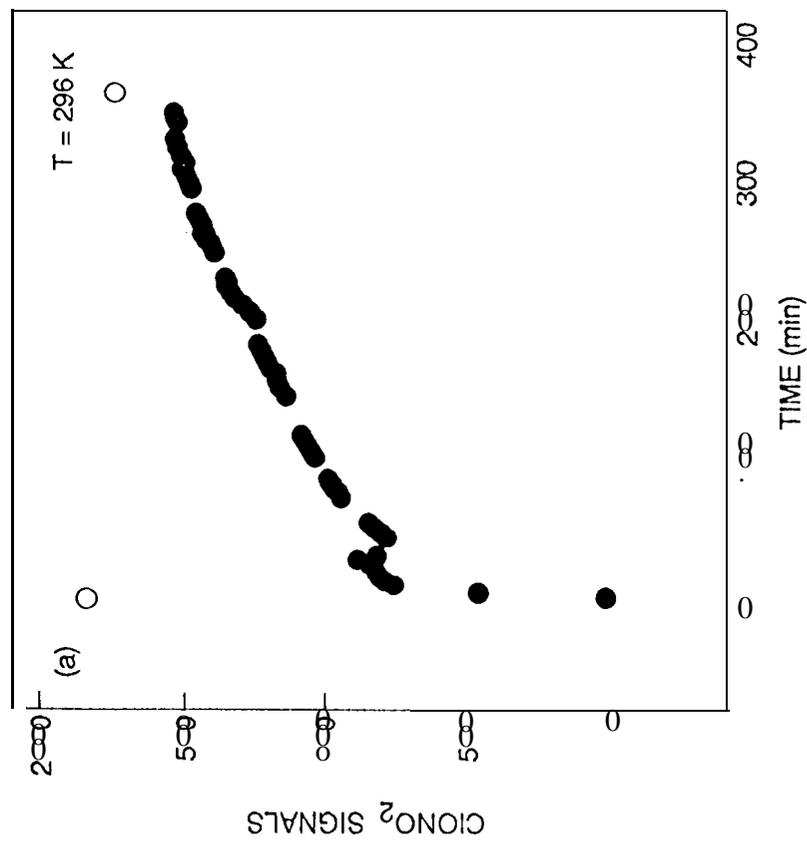


Fig. 4

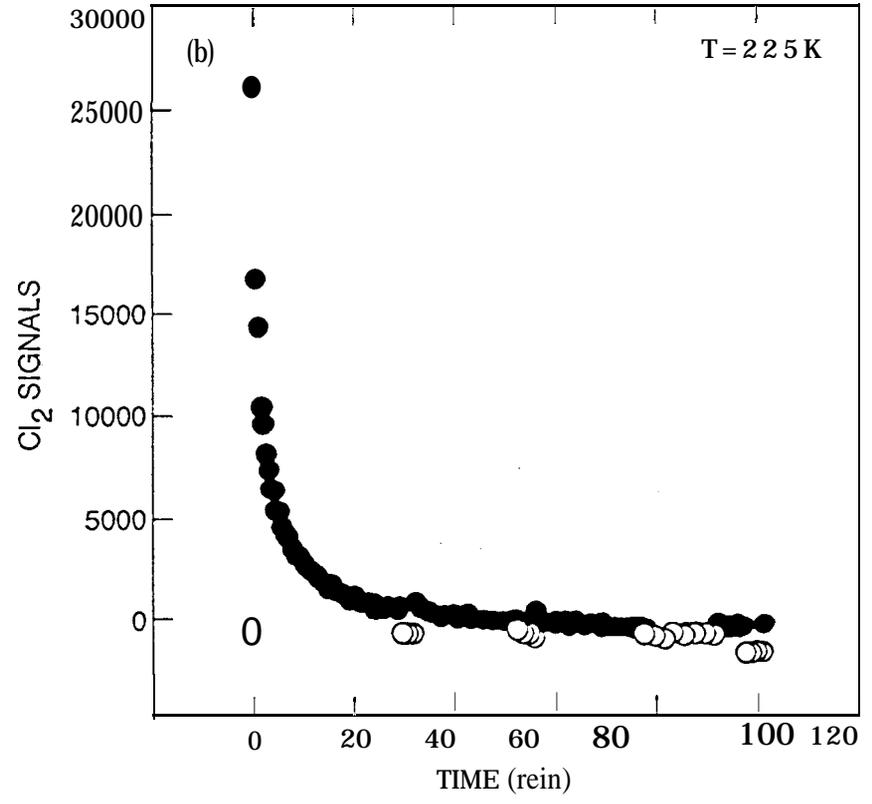
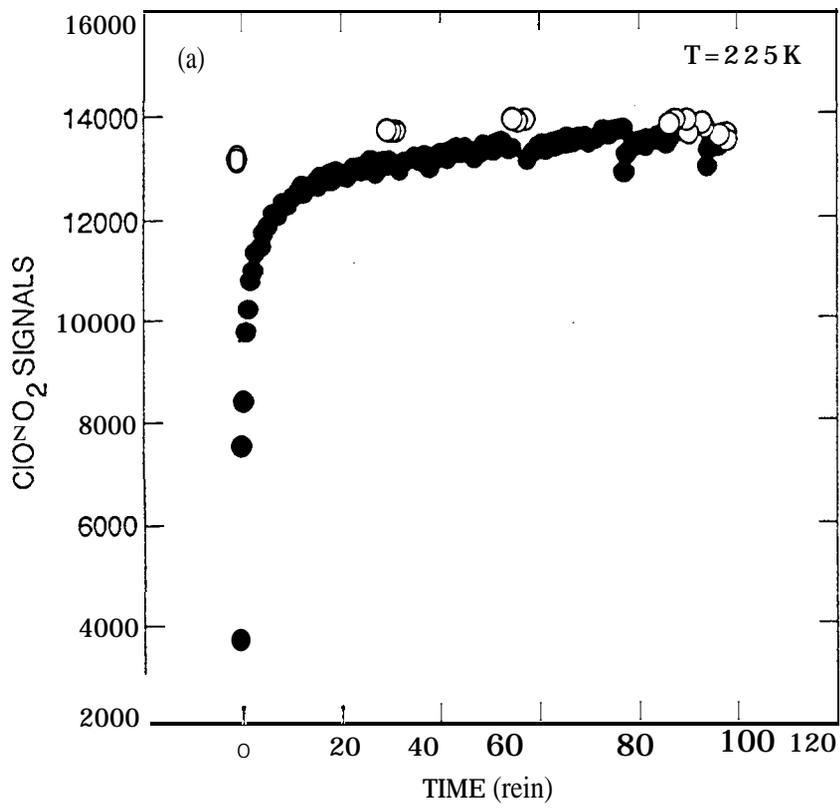


Fig 5

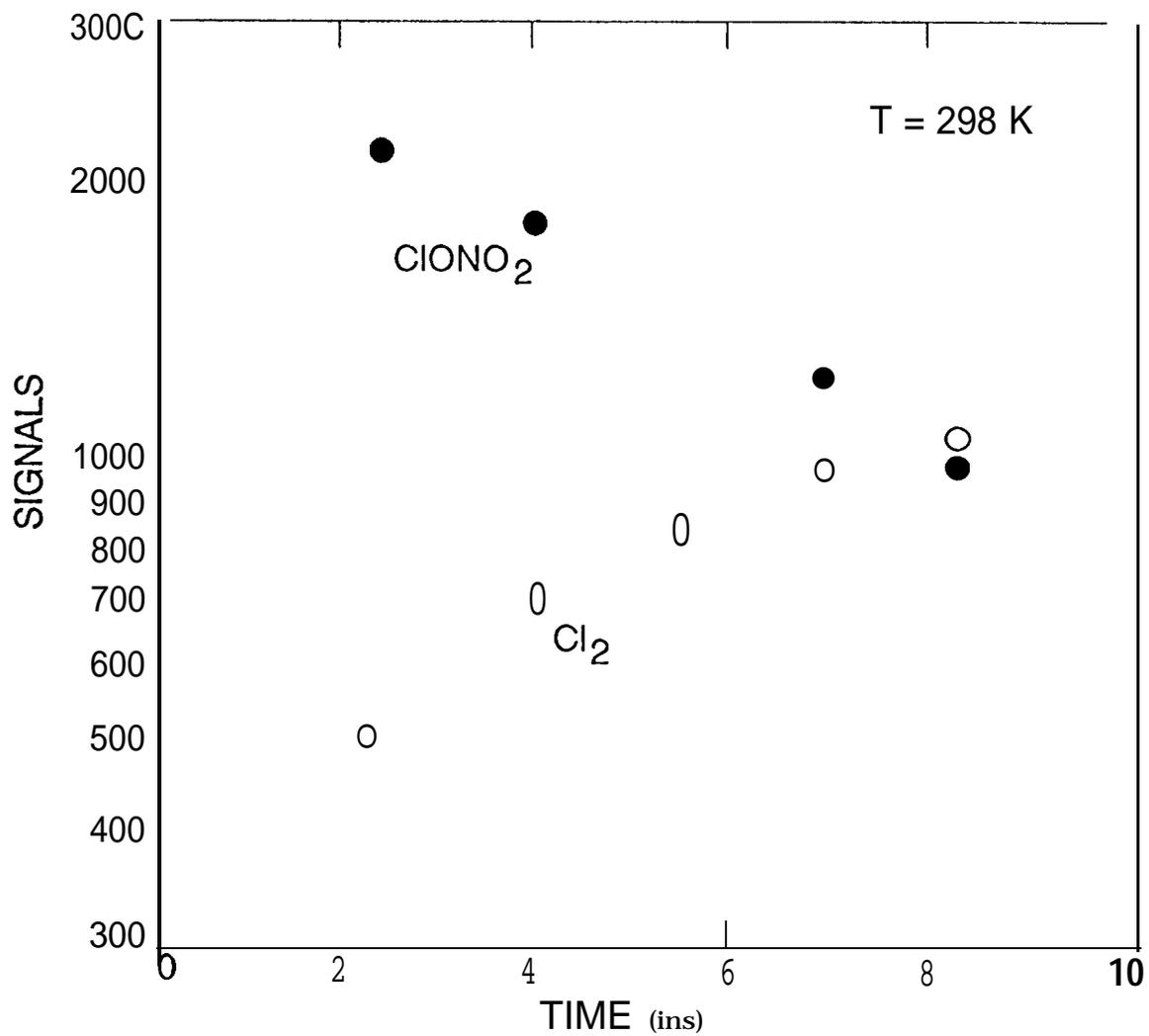
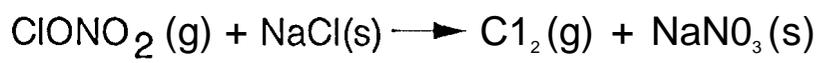


Fig. 6

Table I. Summary of the reaction probability measurements for reaction (1). The total pressure is about 0.300 Torr in all experiments.

<u>ClONO₂</u>	<u>NaCl</u>	<u>T</u>	<u>v</u>	<u>ClONO₂</u>				<u>Cl₂</u>				<u>H₂O</u>	<u>Notes</u>
				<u>k_s</u>	<u>k_g</u>	<u>Y_g</u>	<u>γ_t</u>	<u>k_s</u>	<u>k_g</u>	<u>Y_g</u>	<u>γ_t</u>		
Torr	g	K	cm/s	s ⁻¹	s ⁻¹	x10 ⁻³	X1 0-3	s ⁻¹	s ⁻¹	X1 0-3	X1 0-3	Torr	
2.5 (-8)	15.0	295	1259	66.8	67.2	16.2	1.24	166.1	194.4	39.5	5.11	<2 (-5)	b
				83.9	90.8	21.8	1.96	130.7	147.9	30.1	3.29	<2 (-5)	b
				74.9	80.3	19.2	1.61	116.0	129.5	26.3	2.65	<2 (-5)	b
2.8 (-8)	15.0	296	1239	131.9	150.0	42.4	5.72	173.2	204.8	29.0	3.10	< 2 (-5)	b
				90.7	99.0	28.0	2.93					<2 (-5)	b
				61.8	65.7	18.5	1.52	200.7	243.6	58.3	9.44	< 2 (-5)	b
				98.2	107.9	30.4	3.35	213.4	262.1	62.7	10.6	<2 (-5)	b
1.9 (-6)	15.0	296	1349	60.6	63.8	15.3	1.14	82.0	88.0	17.9	1.44	<2 (-5)	b
				46.7	48.6	11.7	0.78	60.3	63.5	12.9	0.89	<2 (-5)	b
				45.3	47.1	11.3	0.74	62.5	65.9	13.4	0.94	< 2 (-5)	b
				51.9	54.2	13.0	0.90	56.0	58.8	12.0	0.80	< 2 (-5)	b
9.3 (-7)	15.0	297	1412	146.8	165.0	39.8	5.17	196.9	230.8	46.9	6.72	<2 (-5)	b
				129.9	144.1	34.7	4.15	171.0	196.4	40.1	5.24	< 2 (-5)	b
				115.6	126.8	30.6	3.38	101.3	110.0	22.4	2.05	<2 (-5)	b
				110.1	120.3	28.9	3.08	104.0	113.0	23.1	2.15	< 2 (-5)	b
6.7 (-7)	23.0	295	1701	187.0	208.7	44.6	6.20	246.1	284.5	51.5	7.78	<2 (-5)	b
				172.9	191.2	40.8	5.37	184.0	205.1	37.1	4.60	< 2 (-5)	b
				149.2	162.8	34.8	4.15	140.5	152.8	27.7	2.84	< 2 (-5)	b
				133.3	144.1	30.8	3.39	123.5	132.9	24.1	2.36	< 2 (-5)	b
				124.9	134.4	28.7	3.01	131.5	142.2	25.7	2.50	< 2 (-5)	b
2.7 (-7)	15.0	295	1589	122.7	132.9	32.0	3.64	242.6	284.5	58.0	9.37	< 2 (-5)	b

				130.4	141.9	34.2	4.05	177.7	199.7	40.7	5.36	< 2 (-5)	b
				114.3	123.2	29.6	3.21	185.7	209.9	42.8	5.81	< 2 (-5)	b
5.8 (-7)	15.0	295	1693	98.7	104.6	25.1	2.46	190.6	216.2	44.0	6.07	< 2 (-5)	b
				154.8	169.6	40.7	5.36	226.2	258.8	52.6	8.05	< 2 (-5)	b
				134.0	145.0	34.8	4.17	194.5	218.4	44.4	6.16	< 2 (-5)	b
				121.6	130.7	31.4	3.53	151.7	166.1	33.8	3.97	< 2 (.5)	b
2.2 (-7)	15.0	296	1425	85.3	91.3	21.9	1.98	255.0	312.2	63.5	10.8	< 2 (.5)	b
				114.0	124.8	30.0	3.28	192.6	224.6	45.7	6.45	< 2 (.5)	b
				125.5	138.5	33.3	3.88	167.9	192.1	39.1	5.03	< 2 (.5)	b
3.1 (-7)	13.4	296	1466	124.7	132.8	32.9	3.85						b
3.2 (-7)	13.4	296	1469	89.6	93.7	22.2	2.10						b
2.6 (-7)	12.8	296	1522	132.1	140.6	33.9	4.04						b
2.6 (-7)	12.8	296	1524	94.6	99.0	25.3	2.56						b
3.4 (-7)	14.7	296	1565	109.7	115.3	27.7	2.88						b
3.4 (-7)	14.7	296	1539	126.7	134.3	32.3	3.69						b
2.4 (-7)	14.3	296	1226	171.7	194.0	46.7	6.67	159.6	179.7	36.6	4.52		b
2.0 (-7)	14.7	296	1309	215.6	245.3	59.0	9.62	114.9	123.7	25.2	2.47		b
1.4 (-7)	14.8	296	1243	110.4	119.5	28.8	3.07	105.1	113.7	23.2	2.17		b
1.3 (-7)	14.9	296	1295	93.0	98.8	23.8	2.26	165.9	185.1	37.7	4.74		b
1.3 (-7)	14.8	299	1316	76.2	80.1	19.3	1.62	142.0	155.9	31.8	3.60		b
1.3 (-7)	14.5	296	1326	62.6	65.1	15.7	1.18	190.2	214.2	43.7	6.01		b
				89.2	94.4	22.7	2.09						b
2.8 (-7)	14.9	296	1354	161.9	178.7	43.0	5.85						b
				204.5	231.2	55.6	8.77						b
			1372	164.7	181.7	43.7	6.01						b
1.9 (-7)	14.9	298	1407	98.5	104.2	25.1	2.46	79.1	82.8	16.9	1.32		b
3.3 (-7)	5.16	297	1233	135.8	150.0	44.4	7.55	201.1	233.1	58.4	10.7		b
			1236					128.6	141.7	35.5	5.74		b
2.9 (-7)	5.22	296	1252	57.9	60.5	17.9	2.61	36.3	37.4	9.4	1.30		b
			1248	102.7	110.6	32.7	5.21						b
2.6 (-7)	5.18	302	1295	207.5	239.0	70.7	13.7						b
				117.8	128.0	37.9	6.22						b
				130.6	143.1	42.3	7.11						b
1.8 (-6)	15.0	296	1455	67.4	71.0	17.0	1.33	110.9	120.9	24.4	2.35	1.5 (-4)	u
				71.7	75.7	18.2	1.48	80.6	85.8	17.4	1.38	1.5 (-4)	u
5.7 (-7)	15.0	295	1494	93.9	100.6	24.2	2.32	110.9	120.5	24.6	2.38	1.8 (-4)	u
				99.9	107.5	28.5	3.01	102.4	110.6	22.6	2.08	1.8 (-4)	u
				90.8	97.1	23.4	2.19	95.2	102.2	20.9	1.84	1.8 (-4)	u
5.7 (-7)	15.0	298	1461	88.6	94.8	22.8	2.11					1.9 (-4)	u

				88.7	95.0	22.8	2.11	143.1	159.9	32.4	3.71	1.9 (-4)	u
				98.2	105.9	25.4	2.50	130.3	144.2	29.2	3.14	1.9 (-4)	u
								130.6	144.6	29.3	3.16	1.9 (-4)	u
5.4 (-7)	15.0	294	1663	120.0	129.1	31.0	3.45	222.7	255.2	52.1	7.93	6.0 (-5)	u
				123.9	133.5	32.1	3.66	164.1	181.4	37.0	4.60	6.0 (-5)	u
				107.2	114.5	27.6	2.86	153.3	168.4	34.4	4.09	6.0 (-5)	u
2.3 (-7)	23.0	294	1720	162.5	178.2	38.2	4.83	169.6	187.0	34.0	3.99	5.6 (-5)	u
				157.7	172.4	36.9	4.56	178.1	197.3	35.8	4.34	5.6 (-5)	u
				156.9	171.5	36.8	4.54	164.0	180.2	32.7	3.74	5.6 (-5)	u
				143.2	155.3	33.3	3.86	147.4	160.4	29.1	3.08	5.6 (-5)	u
5.9 (-7)	15.0	296	1597	155.2	171.8	41.4	5.51	196.1	223.1	45.5	6.40	5.7 (-5)	u
				143.1	157.1	37.9	4.78	161.8	180.1	36.7	4.54	5.7 (-5)	u
				141.0	154.6	37.2	4.64	142.7	156.8	32.0	3.64	5.7 (-5)	u
2.1 (-7)	8.00	296	1392	114.9	126.2	36.6	5.96	191.5	224.1	55.0	9.89	6.0 (-5)	u
				116.1	127.6	36.9	6.02	194.0	227.6	55.9	10.1	6.0 (-5)	u
				102.4	111.3	32.2	5.12	131.2	146.2	35.9	5.83	6.0 (-5)	u
2.1 (-7)	23.0	296	1722	124.9	134.3	28.8	3.03	200.1	224.8	36.4	4.46	6.8 (-5)	u
				122.8	131.7	28.2	2.93	212.9	241.0	43.8	6.01	6.8 (-5)	u
				108.9	116.0	24.9	2.38	180.8	200.9	36.5	4.47	6.8 (-5)	u
2. I (-7)	23.0	296	1702	79.4	83.2	17.8	1.35	133.8	144.8	26.3	2.61	2.0 (-4)	u
				102.0	108.3	23.2	2.11	148.2	161.9	29.4	3.14	2.0 (-4)	u
				107.5	114.5	24.5	2.31	142.1	154.6	28.1	2.91	2.0 (-4)	u
2.9 (-7)	12.1	296	1377	130.7	139.7	35.7	4.3s	143.4	154.5	33.4	3.94		u
2.5 (-7)	14.4	296	1226	173.9	196.3	47.2	6.79	132.1	145.5	29.7	3.22		u
2.2 (-7)	15.4	296	1224	123.4	135.0	32.5	3.73	151.6	169.8	34.6	4.13		u
1.3 (-7)	14.7	296	1247	128.7	141.1	33.9	3.99	178.8	203.6	41.5	5.53		u
1.3 (-7)	14.7	296	1344	79.0	82.9	20.0	1.71	112.2	120.2	24.5	2.36		u
1.3 (-7)	15.0	297	1327	129.3	140.0	33.7	3.96	124.1	134.2	27.4	2.83		u
3.1 (-7)	5.18	296	1220	148.3	165.6	49.0	8.54	88.5	94.9	28.0	3.80		u
2.0 (-7)	5.14	296	1492	33.6	34.2	10.1	1.40	18.9	19.1	4.8	0.65	3.0 (-3)	u,w
1.7 (-7)	23.0	226	1292	238.4	283.4	69.4	12.3	234.6	278.7	57.8	9.32	<2 (-5)	b
				140.0	154.9	37.9	4.78	260.2	314.9	65.3	11.2	<2 (-5)	b
				105.6	114.0	27.9	2.88	130.6	143.7	29.8	3.20	<2 (-5)	b
				99.4	106.9	26.2	2.60	93.3	99.9	20.7	1.74	<2 (-5)	b
2.8 (-7)	8.00	225	1111	90.8	98.8	32.8	5.23	94.9	104.2	29.3	4.58	<2 (-5)	b
				51.8	54.5	18.1	2.64	109.8	122.3	34.4	5.54	<2 (-5)	b
				28.3	29.1	9.7	1.35	49.0	51.4	14.5	2.07	<2 (-5)	b
1.8 (-7)	14.3	224	981	149.7	165.8	45.6	6.43	195.9	224.5	52.3	7.98		b

2.5 (-7)	14.8	224	1022	127.4	138.1	38.0	4.80	117.3	126.7	29.5	3.19			b
2.0 (-7)	23.0	225	1289	51.0	52.9	13.0	0.81	116.5	127.0	26.3	2.61	3.0	(-4)	u
				49.7	51.5	12.6	0.78	139.8	154.9	32.1	3.64	3.0	(-4)	u
				88.5	94.5	23.1	2.10	115.1	125.2	26.0	2.56	3.0	(-4)	u
1.9 (-7)	23.0	225	1354	60.0	62.5	15.3	1.06	120.3	130.6	27.1	2.74	2.1	(-4)	u
				57.3	59.6	14.6	0.98					2.1	(-4)	u
				79.2	83.6	20.4	1.70	89.0	94.6	19.6	1.59	2.1	(-4)	u
				36.6	37.5	9.2	0.48					2.1	(-4)	u
9.0 (-8)	23.0	225	1325	74.2	78.2	19.1	1.57	171.6	193.7	40.2	5.24	1.3	(-4)	u
				76.5	80.7	19.7	1.60	99.9	107.2	22.2	1.95	1.3	(-4)	u
				72.8	76.6	18.8	1.49	105.8	114.0	23.6	2.16	1.3	(-4)	u
				67.5	70.8	17.4	1.30	61.0	63.6	13.2	0.83	1.3	(-4)	u
9.6 (-8)	23.0	225	1299	70.4	74.0	18.2	1.41	237.3	281.9	58.5	9.49	1.0	(-4)	u
				116.4	126.6	31.0	3.43	218.3	255.8	53.1	8.17	1.0	(-4)	u
				57.8	93.6	22.9	2.06	151.8	169.5	35.2	4.23	1.0	(-4)	u
				77.9	82.4	20.1	1.66	155.3	173.8	36.0	4.38	1.0	(-4)	u
2.6 (-7)	14.6	223	989	117.5	127.3	35.0	4.20	123.3	134.5	31.3	3.51			u

Notes:

- b. NaCl substrates were baked at temperatures up to 473 K overnight.
- u. NaCl substrates were not baked.
- w. A partial H₂O pressure of 3 x 10⁻³ Torr was admitted into the flow reactor. The reaction ClONO₂ + H₂O → HOCl + HNO₃ is more important than reaction (1). See text for details.

Table II. Summary of the reaction probability measurements for reaction (1). The uncertainties represent one standard deviation.

<u>Temperature</u>	<u>NaCl Substrate</u>	<u>Number of Experiments</u>	<u>$\gamma_1(\text{ClONO}_2)$</u>	<u>Number of Experiments</u>	<u>$\gamma_1(\text{Cl}_2)$</u>	<u>relative</u>
298	aqueous	25	$(4.3 \pm 2.95) \times 10^{-3}$	7	$(5.3 \pm 3.14) \times 10^{-3}$	$(4.63 \pm 3.05) \times 10^{-3}$
298	unbaked with water vapor	17	$(3.79 \pm 2.07) \times 10^{-3}$	6	$(4.34 \pm 2.14) \times 10^{-3}$	$4.07 \pm 2.0 \times 10^{-3}$
225	baked	4	$(7.9 \pm 3.48) \times 10^{-3}$	4	$(6.27 \pm 2.86) \times 10^{-3}$	$(6.73 \pm 3.17) \times 10^{-3}$
225	unbaked with water vapor	5	$(8.1 \pm 1.37) \times 10^{-3}(b)$	5	$(4.72 \pm 2.87) \times 10^{-3}$	$(4.72 \pm 2.87) \times 10^{-3}$

Notes:

- The average value is calculated from the data based on the ClONO_2 decay rates and the Cl_2 growth rates.
- This result is considered to be unreliable because of the interference due to the reaction $\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$ text for details.